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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 2/38	A1	(11) International Publication Number: WO 98/50436 (43) International Publication Date: 12 November 1998 (12.11.98)
(21) International Application Number: PCT/AU98/00337 (22) International Filing Date: 8 May 1998 (08.05.98) (30) Priority Data: PO 6696 8 May 1997 (08.05.97) AU (71) Applicant (for all designated States except US): UNISEARCH LIMITED [AU/AU]; 221-227 Anzac Parade, Kensington, NSW 2033 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): DAVIS, Thomas [AU/AU]; 38 Earl Street, Randwick, NSW 2031 (AU). GILBERT, Robert [AU/AU]; Unit 77/19 Queen Street, Newtown, NSW 2042 (AU). KUKULJ, Dax [AU/AU]; 75 Fourteenth Avenue, West Hoxton, NSW 2171 (AU). (74) Agent: F.B. RICE & CO.; 605 Darling Street, Balmain, NSW 2041 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYMERISATION REACTIONS UNDER MINIEMULSION CONDITIONS		
(57) Abstract		
<p>A method of forming a polymer comprising: a) forming a miniemulsion including i) a monomer, ii) a non-aqueous solution including a cobalt-containing chain transfer agent, and iii) an aqueous solution; and b) reacting the miniemulsion in the presence of an initiator for a time sufficient to form the polymer.</p>		

Polymerisation reactions under miniemulsion conditions

Technical Field

The present invention relates to a method for the formation of polymers by emulsion polymerisation and in particular to the formation of
5 polymers under miniemulsion conditions.

Background Art

Emulsion polymerisation is widely used as a commercial process to produce a variety of latexes for a range of industries. Emulsion polymerisation processes are typically used to produce high molecular
10 weight polymers, however, in recent times the advantage of generating much lower molecular weights for specific product applications has become evident. Catalytic chain transfer has been shown to be a highly effective synthetic tool for reducing molecular weight in free-radical solution/bulk polymerisation and emulsion polymerisation.

15 Limitations to the use of catalytic chain transfer agents in emulsion polymerisation reactions have been identified in the prior art. Firstly, such polymerisation reactions result in a loss of catalytic activity with time. This has, for example, been noted where cobaloximes are used as catalytic chain transfer agents. In addition, it has been noted that initiators which form
20 oxygen centred peroxide radicals have a detrimental effect on the reaction, causing destruction of the catalyst. Similar behaviour has also been seen for oxygen centred persulfate radicals. This latter problem is highly inconvenient for commercial application of the technology, as persulfates are often the initiator of choice.

25 The present inventors have surprisingly found that one way of addressing the problem in the prior art is to separate the chain transfer agent from the primary initiator radicals by operating the chain transfer polymerisation reaction under miniemulsion conditions.

In miniemulsion polymerisation, the initial monomer droplet size, of
30 about 100 nm is much smaller than conventional emulsion polymerisation, which is about 1 μ m in size. Due to this size difference, particle nucleation occurs predominantly in the monomer droplets as opposed to creating a new particle phase.

generating free radicals in an aqueous or organic phase may be used in the present invention. Suitable initiators include peroxides, persulfates, azo initiators and redox initiator systems. Preferable persulfate initiators include potassium persulfate (KPS), ammonium persulfate, sodium persulfate.

- 5 Preferable azo initiators include azobisisobutyronitrile (AIBN), azobiscyanovaleric acid and azobis(2-amidinopropane)dihydrochloride (Vazo V50TM). Preferable redox initiators include a redox couple from which each member is selected from iron catalysts, sodium metabisulfite and sodium formaldehyde sulfonate. Particularly preferred are initiators that generate
10 oxygen centred radicals such as, persulfates and peroxides.

The concentration of the initiator used will depend on many variables including temperature, monomer and other reaction conditions. The appropriate concentrations to be used falls within the skill of a formulator of polymers.

- 15 AIBN produces carbon-centred radicals while KPS produces oxygen centred radicals. When AIBN is used as initiator, it is preferably added to the aqueous phase, prior to the formation of the miniemulsion, while KPS is preferably predissolved in water and added in the miniemulsion at the reaction temperature.

- 20 The emulsion may be stabilised by the presence of a highly water-insoluble compound (hydrophobe). A possible role of the hydrophobe is to minimise the Ostwald ripening effect (diffusion of the oil phase from small to large droplets to reduce the interfacial free energy of the system). The hydrophobe is preferably contained in the non-aqueous solution. The
25 hydrophobe may be selected from a variety of alkanes and fatty alcohols, however, it will be appreciated that a suitable hydrophobe can be selected from a wide variety of other species. Preferably the alkane is hexadecane and the fatty alcohol is cetyl alcohol

- An advantage of miniemulsion polymerisation is that highly water
30 insoluble ingredients are present directly in the monomer droplets which are the locus of polymerisation, whereas in conventional emulsion polymerisation, monomer and other reaction components need to diffuse from the droplets via the water phase to the locus of the reaction (the particles). This can be exploited by dissolving highly water insoluble chain
35 transfer agents directly into the monomer droplets, the loci of the reaction.

Figure 2 is a graph showing dependence of M_n vs conversion on the concentration of catalyst (COBF and CPhBF) for AIBN initiated runs.

Figure 3 is a graph showing dependence of conversion vs time on the concentration of catalyst (COBF and CPhBF) for AIBN initiated runs.

5 Figure 4 is a graph showing dependence of M_n vs conversion on the concentration of catalyst (COBF and CPhBF) for KPS initiated runs.

Figure 5 is a graph showing dependence of conversion vs time on the concentration of catalyst (COBF and CPhBF) for KPS initiated runs.

Modes for Carrying Out the Invention

10 The following Examples further illustrate the present invention.

Six examples of miniemulsion polymerisation of methyl methacrylate using two different initiators (AIBN and KPS) and two different cobalt-containing chain transfer agents (COBF and CPhBF) have been described. The recipes for the miniemulsion polymerisation reactions carried out
15 according to Examples 2 to 5 and 7 to 8 are outlined in Tables 1 and 2.

Table 1: Typical recipe for miniemulsion polymerisation reactions

Component	Mass/g
water	80
sodium dodecylsulfate	0.80
methyl methacrylate	20
hexadecane	0.50
initiator: AIBN or KPS	0.20
Catalyst: COBF or CPhBF	see Table 2

General procedure

20 Typically, the miniemulsion was formed by the following procedure. The surfactant, sodium dodecylsulfate (SDS), was dissolved in deionised water that was previously deoxygenated by purging with argon for one hour. The cobalt-containing chain transfer agent was dissolved in a non-aqueous solution comprising methyl methacrylate (MMA) and the hydrophobe
25 (hexadecane), that were previously degassed by three freeze-pump-thaw cycles. The monomer solution was transferred via a cannula to the aqueous solution and initial emulsification was achieved using a magnetic stirrer.

Table 2: Summary of Runs

Examples	Run	Initiator	Catalyst	Concentration ^{a)}
1	A1	AIBN	-	-
2	A2	AIBN	COBF	3.0
3	A3	AIBN	COBF	18
4	A4	AIBN	COPhBF	2.0
5	A5	AIBN	COPhBF	9.3
6	K1	KPS	-	-
7	K2	KPS	COBF	17
8	K3	KPS	COPhBF	2.0

^{a)} ppm mol/mol. equivalent to $[S]/[M] \times 10^6$, where [S] is the concentration of catalytic chain transfer agent and [M] is the monomer concentration.

5

Results from azobisisobutyronitrile (AIBN) Initiated Polymerisation

The influence of cobalt containing chain transfer agents on the miniemulsion polymerisation of MMA initiated by AIBN can be seen in Figures 2 and 3. The control polymerisation (run A1 with no chain transfer agent) produces a number average molecular weight, M_n , in the order of 10^6 which is typical of a miniemulsion polymerisation. Upon the addition of 3.0 and 18 ppm COBF the molecular weight of PMMA is drastically reduced to 87.0×10^3 and 4.41×10^3 respectively. A similar trend is noted for the COPhBF mediated reactions with an even greater reduction in molecular weight to 18.4×10^3 and 1.10×10^3 for a slightly lower concentrations of 2.0 and 9.3 ppm.

The first significant feature is that COPhBF appears to be a more effective catalyst than COBF under these conditions. This can easily be explained by the relative solubilities of the chain transfer agents in the two phases. It has been shown that COBF partitions approximately equally between the oil and water phase. Thus for the same overall catalyst concentration, the COBF concentration in the locus of polymerisation is less than the COPhBF concentration which resides exclusively in the oil phase.

Another important point to make is that all these reactions were performed in batch and in the case of COPhBF mediated polymerisation (run A4) the efficiency of the transfer process was maintained throughout the reaction to high conversion. This contrasts with previous emulsion studies

Table 3: Summary of final properties from each run

		Molecular weight Distribution Averages (MWD)			Particle size Distribution Averages (PSD)^a (nm)			
Run	Conv^b	M_n	M_w	PDi	D_n	D_w	PDi	N_c
A1	0.94	828x10 ³	2.12x10 ⁶	2.6	81	96	1.19	6.14
A2	0.65	87.0x10 ³	171x10 ³	20	96	135	1.41	3.69
A3	0.34	4.14x10 ³	10.8x10 ³	2.4	-	-	-	-
A4	0.92	18.4x10 ³	116x10 ³	6.3	85	125	4.47	5.23
A5	0.20	1.10x10 ³	3.76x10 ³	3.4	-	-	-	-
K1	0.99	900x10 ³	2.3x10 ⁶	2.6	77	86	1.12	7.15
K2	0.96	157x10 ³	436x10 ³	2.8	71	76	1.07	9.12
K3	0.93	17.0x10 ³	52.3x10 ³	3.1	77	84	1.09	7.15

^a Omitted samples did not go to high enough conversion to be measured by CHDF

^b Conversion of final sample taken

M_n Number average molecular weight

M_w Weight average molecular weight

PDi Polydispersity

10 D_n Number average diameter in nm

D_w Weight average diameter in nm

N_c Concentration of latex particles in L⁻¹

15 It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

12. The method according to claim 11 wherein the cobalt containing chain transfer agent is tetraphenyl cobaloxime boron fluoride (COPhBF).
13. The method according to any one of claims 1 or 12 wherein the initiator is included prior to formation of the miniemulsion.
- 5 14. The method according to any one of claims 1 or 12 wherein the initiator is included after formation of the miniemulsion.
15. The method according to any one of claims 1 or 14 wherein the initiator is selected from the group consisting of peroxides, persulfates, azo initiators, and redox initiators.
- 10 16. The method according to claims 15 wherein the persulfate initiator is selected from the group consisting of potassium persulfate (KPS), ammonium persulfate, and sodium persulfate.
17. The method according to claim 15 wherein the azo initiator is selected from the group consisting of azobisisobutyronitrile (AIBN),
- 15 azobiscyanovaleric acid, and azobis(2-amidinopropane)dihydrochloride.
18. The method according to claim 15 wherein the redox initiator is selected from the group consisting of iron catalysts, sodium metabisulfate and sodium formaldehyde sulfonate.
19. The method according to any one of claims 1 to 18 wherein the
- 20 aqueous solution includes of one or more surfactants.
20. The method according to claim 19 wherein the surfactants are selected from the group consisting of anionic, cationic and non-ionic surfactants.
21. The method according to claim 20 wherein the surfactant is sodium dodecylsulfate (SDS).
- 25 22. The method according to any one of claims 1 or 21 wherein the reaction is controlled isothermally at 65°C and ambient pressure.
23. A polymer prepared by the method according to any one of claims 1 to 22.

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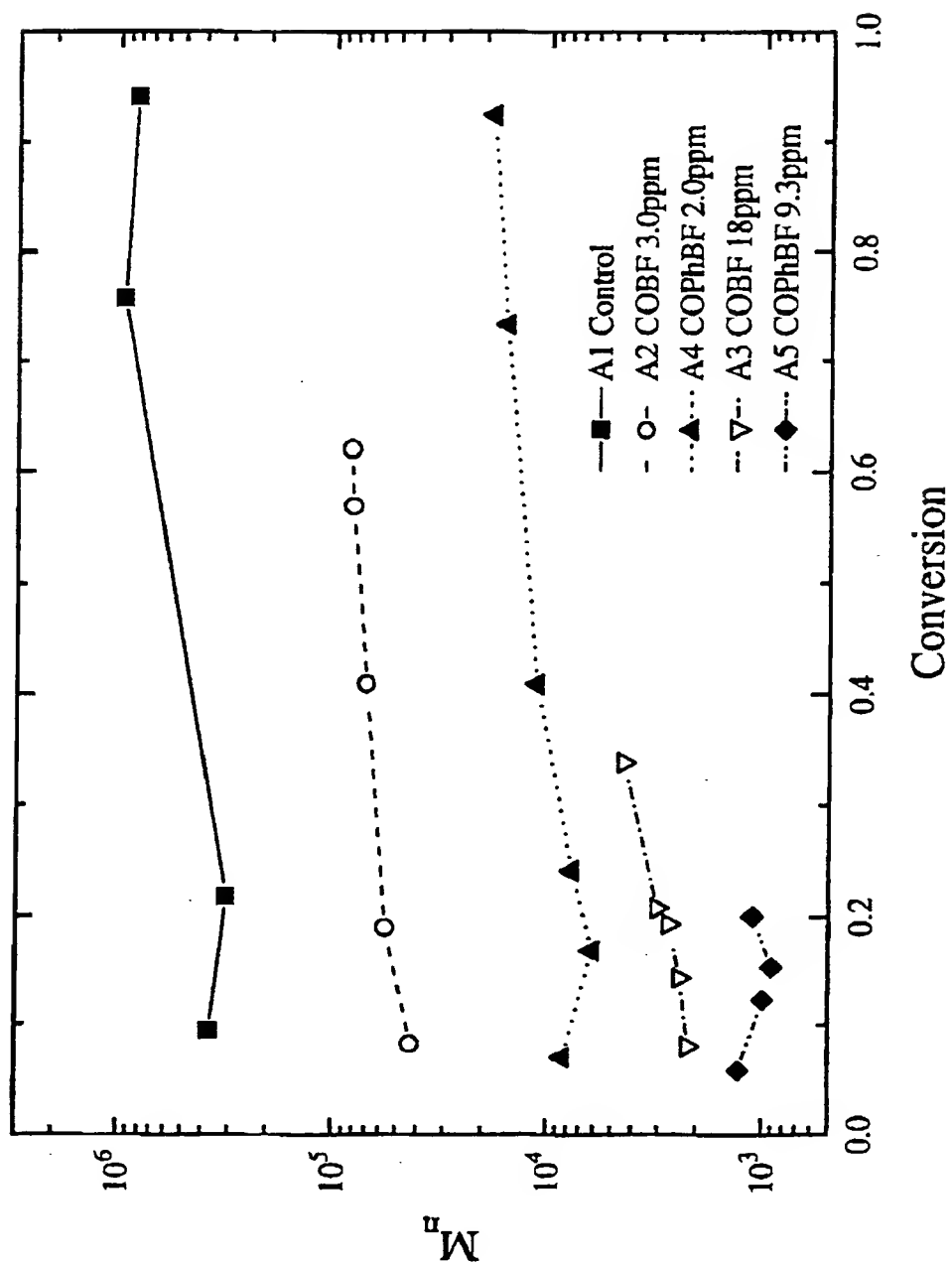
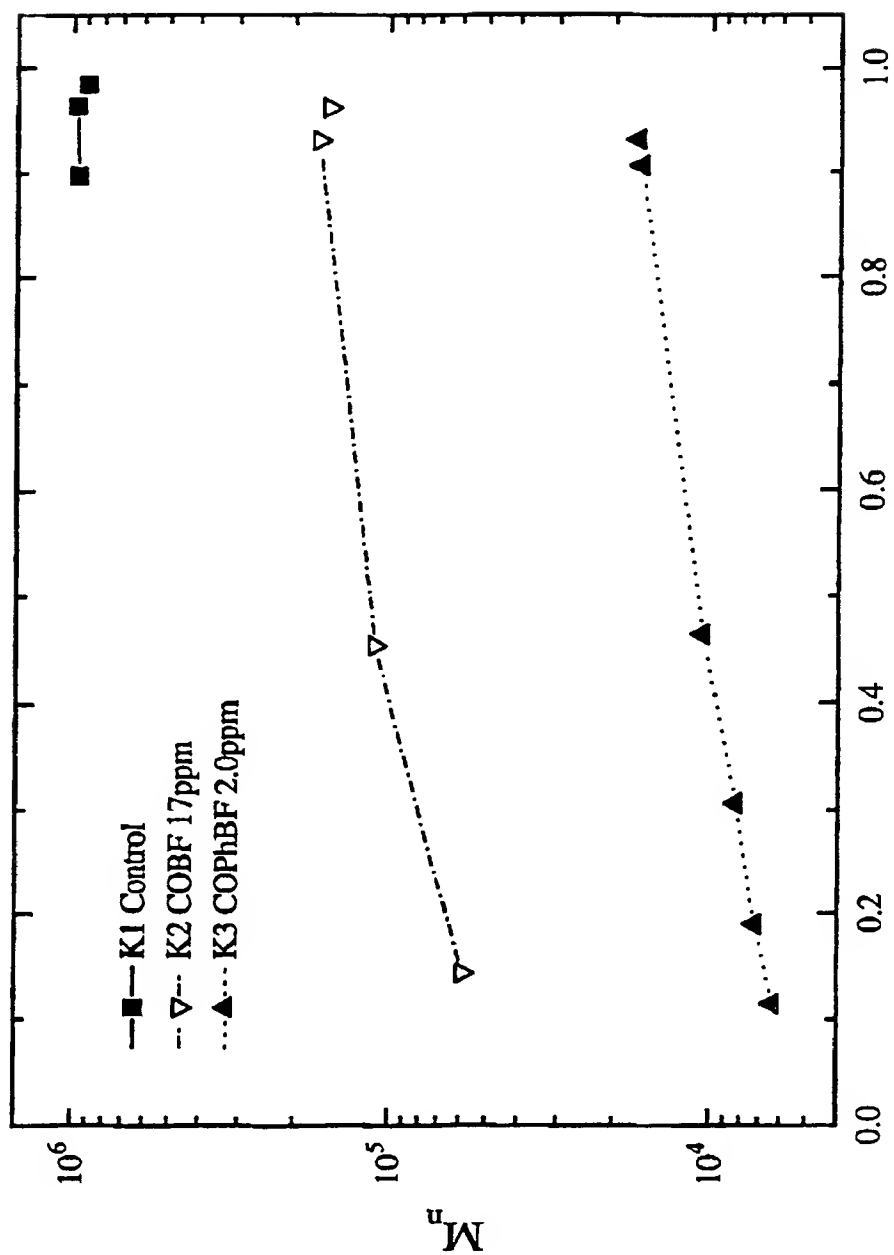


Figure 2

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Conversion
Figure 4

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 98/00337

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C08F 2/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC C08F 2/38, 2/40, 2/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT: EMULSION POLYMER:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96/15158 A (E.I. DU PONT DE NEMOURS AND COMPANY et al.) 23 May 1996 whole document	1-23
A	EP, A, 199 436 (E.I. DU PONT DE NEMOURS AND COMPANY) 29 October 1986 whole document	1-23
A	US, A, 5 326 843 (ROHM & HAAS CO.) 5 July 1994 Abstract	1-23

☐ Further documents are listed in the
continuation of Box C

☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
12 June 1998

Date of mailing of the international search report
22 JUN 1998

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	WO 98 50436 A (UNISEARCH LTD) 12 November 1998 (1998-11-12) ---		C08F2/22 C08F2/38
A	WO 96 15158 A (E.I.DU PONT DE NEMOURS AND CO.) 23 May 1996 (1996-05-23) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 1 March 2001	Examiner Cauwenberg, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 00 0002

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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